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Electroplating Cobalt-60 Without Residue*

by

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A method of electroplating cobalt-60 to produce millicurie standard sources has been described by Caldwell and Graves¹. However, our problem

¹ "Secondary Standard Co-60 Sources Prepared by Electrodeposition." Paul A. Caldwell and J. D. Graves, Nucleonics 13(12) Dec. 1965, p. 49.

~~was to produce several tons of 1/8 inch diameter magnetic pellets with uniformly contained Co-60 at the level of 1.0 ± 0.2 curie per pound, and this procedure was hardly suitable for the task.~~ Since these radioactive pellets were to be mechanically handled their protection against abrasion and corrosion was necessary. This was accomplished by plating a layer of nickel over the cobalt followed by a layer of cadmium on the outside of the pellet.

Plating Process

A barrel plating operation using the "Udylite Handiplater" and 50 pounds of pellets per batch was developed. The 50 pound batch was dictated by the fact that the Co-60 was supplied in packaged units of 25 ± 2 curies of contained Co-60 in neutron irradiated cobalt disks 0.4 inches diameter by 0.08 inches thick. The barrel plater would handle 50 pounds of spherical steel pellets², which would use two packages of Co-60 containing disks per

² Carbon steel balls, short headed, rough ground, unhardened, 1/8 inch diameter, are obtainable from the ball bearing industry.

lot.

* Work done under contract DA-42-007-403-cml-453, Army Chemical Corps.

The cobalt electrolyte was a solution of cobalt sulfate at pH = 3.5. Such an electrolyte is sufficiently acid to dissolve iron readily from the uncoated iron pellets when these are below the active cathodic surface of the pellet mass in the barrel plater. Iron hydroxide in the electrolyte was found to interfere with the electroplating of cobalt. At pH > 2.8 iron in solution is largely precipitated as a hydroxide and can be continuously removed from the electrolyte by filtration. Nevertheless, to keep the accumulation of the precipitated iron hydroxide in the electrolyte low and to promote adhesion of the cobalt plate, the iron pellets were first plated with a 0.25 mil copper layer before being plated with cobalt.

DETAILS OF THE PLATING OPERATION

The cobalt, nickel, and cadmium plating must be done remotely from the operators because of the gamma radiation from the cobalt-60. The operation accordingly was devised to be conducted in a large radiation cell, or "cave", equipped with various remote manipulators.

In electroplating a metal it is usual to use an active anode of the metal to be plated. This was not feasible in our problem for an anode of cobalt containing cobalt-60 would have to be cast from the molten metal, and this would lead to a radioactive scrap, both in the casting processes and in the plating operation. An inert lead anode therefore was used and the electrolyte was continuously replenished with cobalt from a cobalt carbonate slurry.

The following chemical reactions are involved:

1. cathode reaction: $\text{Co}^{++} + 2\text{e}^- \rightarrow \text{Co}$ (plated out)
2. anode reaction: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2$ (gas) + 2e^-
3. overall reaction: $\text{H}_2\text{O} + \text{Co}^{++} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2$ (gas) + Co (plated out)

The cobalt ion plated out of the electrolyte is replaced in the electrolyte by a chemical equivalence of hydrogen ions.

Few, if any, electrolytic processes are entirely free from side reactions; however, in this case none were thought likely to interfere with the cobalt plating operation as proposed. Cobalt intended for each batch of pellets is made into a cobalt carbonate³ slurry and metered to the electro-

³ Although the material is a basic carbonate of variable composition the chemistry, for our purposes, is equivalent to that of pure cobalt carbonate and will be referred to throughout this report as cobalt carbonate.

lyte at such a rate as to keep its pH constant⁴. Thus the Co⁺⁺ content of

⁴ The electrolyte could also be kept at constant Co⁺⁺ concentration by maintaining the γ activity of the solution constant, provided the ratio of Co-60 to total Co content of the slurry is kept constant. Since the pH is a logarithmic function of H⁺ concentration and γ activity is a linear function of Co-60 content, the monitoring of the electrolyte by gamma radiation would be the more sensitive method

the electrolyte is kept substantially constant.

The chemistry of the cobalt carbonate addition is

4. Carbonate reaction: $\text{CoCO}_3 + 2\text{H}^+ \rightarrow \text{Co}^{++} + \text{H}_2\text{O} + \text{CO}_2 \text{ (gas)}$
5. Electrode reaction: $\text{H}_2\text{O} + \text{Co}^{++} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2 \text{ (gas)} + \text{Co (plated)}$
6. Overall reaction: $\text{CoCO}_3 \rightarrow \text{CO}_2 \text{ (gas)} + 1/2 \text{O}_2 \text{ (gas)} + \text{Co (plated)}$

This chemistry is ideal for the solution of our problem, and the remote manipulation of the process is not difficult. Furthermore, all the cobalt-60 can be plated out with substantially no radioactive scrap. Even the last portions of cobalt can be plated from the electrolyte by substituting an active nickel anode at the end of the process. This comes about because

cobalt-nickel alloys are readily platable as coherent films at all compositions, and cobalt ion is selectively plated⁵ out in preference to nickel ion.

⁵ "Electrodeposition of Cobalt Base Alloys--" Interim Technical Report. Contract DA-04-495-505-ORD-862-500-1 WAL File No. 317/6-1. Ordnance Project No. TR 3-3003. Department of Army Project No. 5 ROI-01-004. July 31, 1957 by W. Martin Fassell, Jr., and John P. Baur.

Thus the cobalt ions in the electrolyte will gradually be replaced by nickel ions and the plated alloy layer of sufficient thickness will contain substantially all of the cobalt-60.

The concentration of Co-60 in the disks varied greatly, the least active disk containing 2.38 grams of cobalt per curie of Co-60. At this concentration a plated cobalt layer to give 1 curie of Co-60 per pound of plated pellets would be 0.0964 mil thick. To accommodate this fact a cobalt layer of 0.125 mil thickness was chosen as the cobalt layer to be applied to the pellet. To obtain this, natural cobalt in the form of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the dissolved active cobalt disks so that the cobalt necessary to coat one pound of pellets with a 0.125 mil thick layer (3.086 grams) would contain 1 curie of Co-60.

The plating operation, as developed, required 7.5 gallons of electrolyte at pH = 3.5 at the beginning of the batch run. During the run 3 gallons of CoCO_3 slurry carrying the exact amount of cobalt to be plated out in the run was metered into the electrolyte so as to hold the pH constant at a value of 3.64. This value of pH was chosen because at the end of the run there will be 10.5 gallons of electrolyte, and if the total Co^{++} ion content (not concentration) of the electrolyte at the end of the run is to be equal to that at the beginning of the run, the pH of the electrolyte will have changed from 3.64 to 3.50 due to the dilution resulting from the addition of the

CoCO_3 slurry.

After plating each lot of pellets the Co^{++} in the residual electrolyte was precipitated as CoCO_3 . By a decantation process the soluble salts resulting from the precipitation could be largely removed and the volume of the electrolyte could be brought back to its original volume of 7.5 gallons and its original Co^{++} concentration.

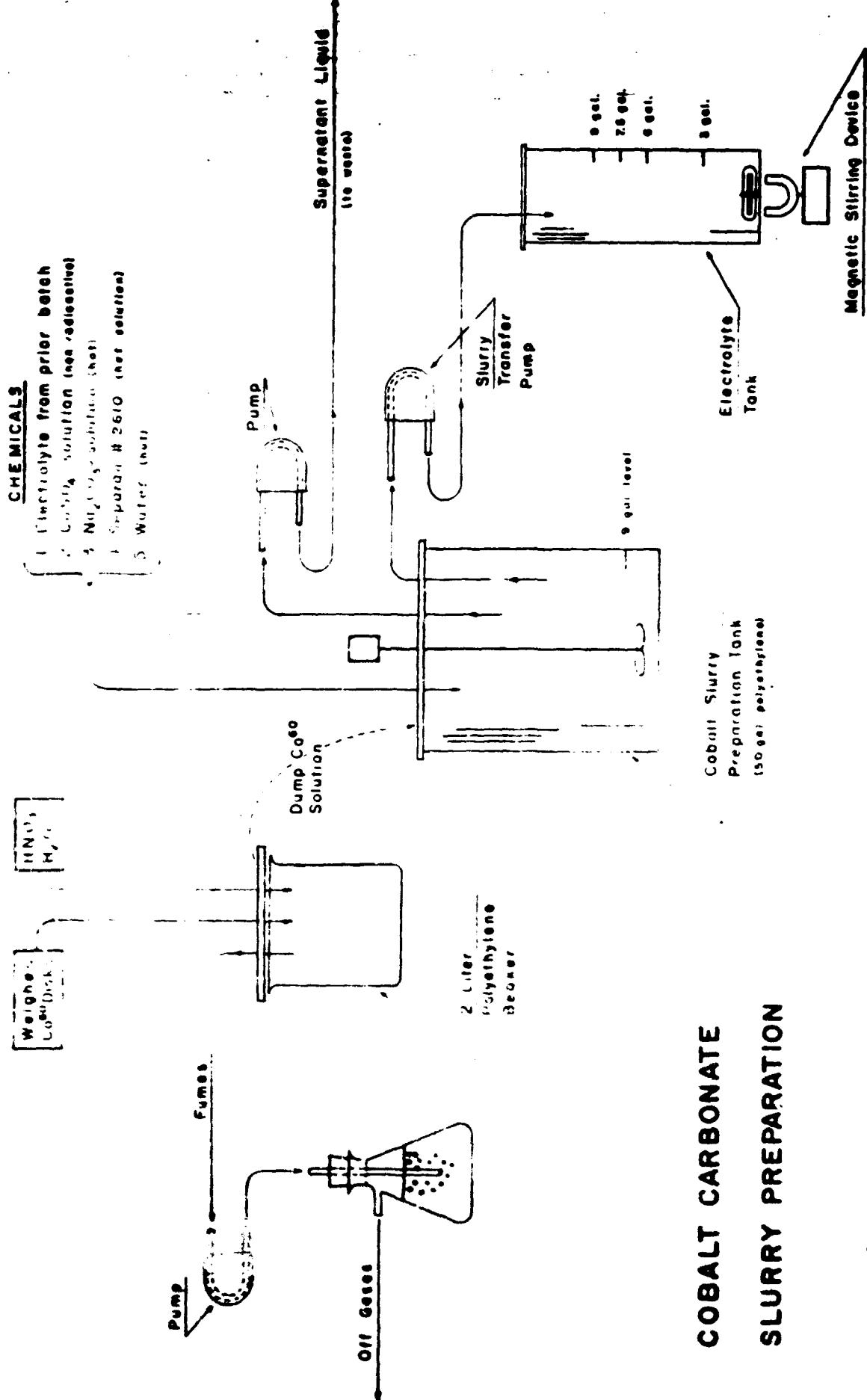
Preparation of the Initial Lot of Cobalt Carbonate Slurry

The original batch of cobalt carbonate slurry was made by taking the active cobalt disks from 6 packages (150 curies of contained Co-60), weighing the cobalt disks, and transferring them to a 2000 l. high-density polyethylene beaker, Figure 1, where they are dissolved in 5 ml of concentrated nitric acid plus 1.7 ml of water per gram of cobalt in the disks.

The dissolution of the cobalt by the acid is an active process with copious fumes. If Co-60 entrained in the fumes is a problem a loose fitting lid can be placed on the beaker and fumes drawn by an aspirator from the beaker through a sodium carbonate wash solution to catch the cobalt. This wash can later be introduced into the process during the precipitation of the cobalt as carbonate, so that no active Co-60 is lost due to fuming at the time of solution of the metal.

The concentrated cobalt nitrate solution is then dumped into the cobalt slurry preparation tank, Figure 1, and concentrated cobalt solution (made from assayed commercial $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) added so as to bring the total cobalt in this tank to 462.9 grams.

To precipitate the cobalt as carbonate a hot concentrated solution of 2900 grams of sodium carbonate⁶ is added. Two liters of hot solution



⁶ Sidgwick ("Chemical Elements and Their Compounds", Vol. II, p. 1381) gives the solubility of CoCO_3 as 3.73 mg. per liter at 15°C . From this datum we calculate a solubility product of 5.3×10^{-10} . We could wish the solubility were less. However, this solubility is not such as to make our process impractical and if significant quantities of cobalt-60 are lost in the wash water resulting from the carbonate precipitation this can be recovered by precipitating as a sulfide, or perhaps as an oxalate, where the solubility product is much less than with the carbonate.

of #2610 Dow Separan (2 gms per liter) is then added to flocculate the precipitated cobalt carbonate. After stirring this concentrated slurry for five minutes the tank is filled with hot water (at not less than 150°F). (This order of procedure is important for good flocculation.) Under these conditions the precipitate will settle in approximately 30 minutes to a slurry whose volume is less than nine gallons. The supernatant liquid is then pumped off.⁷

⁷ It was found that peristaltic type pumps were well suited to the many services required of pumps in this process. These pumps use a smooth "Tygon" (polyvinyl) tube which can be quickly flushed clean of any Co-60 residue. These are self priming, will pump gases, liquids, and slurries. New "Tygon" tubes can be quickly inserted. Furthermore, the capacity of the pumps can be quickly altered by adjusting the speed of the motor. Gamma radiation darkens the "Tygon" tubing and slowly stiffens them; however, these tubes can be changed frequently so that no difficulty from spilled solutions containing Co-60 need arise because of tube breakage after extended use.

Five successive decantation operations (perhaps fewer) will reduce the concentration of dissolved salts to an acceptable level for a successful cobalt plating operation.⁸ The preparation of the cobalt carbonate slurry

⁸ Flocculation and settling is not satisfactory if the solution is cold. Other methods, such as filtering and centrifuging, were attempted to speed up this process, but were not successful, nor are they as safe from radiation hazard as decantation.

can be completed in 2-1/2 hours. After the final washing the slurry, which now has a volume somewhat less than 9 gallons, is pumped to a tall poly-

ethylene tank of about 12 gallons capacity which has been marked at the 3, 6, 7-1/2, and 9 gallon levels. This vessel is referred to as the "electrolyte tank", Figures 1 and 2. Distilled water is then added to the electrolyte tank to make the slurry volume exactly 9 gallons. The contents are then stirred to uniformly disperse the precipitated cobalt carbonate in the slurry.

Three gallons of the uniform slurry are then pumped to the "slurry tank", Figure 2. Six gallons of slurry remain in the electrolyte tank. The quantities have been so chosen that the cobalt slurry in the electrolyte tank contains 100 curies of Co-60 and the slurry in the slurry tank contains 50 curies of Co-60, which is the necessary amount to plate a 50 pound batch of pellets with a cobalt layer containing 1 curie of Co-60 per pound of pellets.

Preparation of the Cobalt Slurry for a Succeeding Batch of Plated Pellets

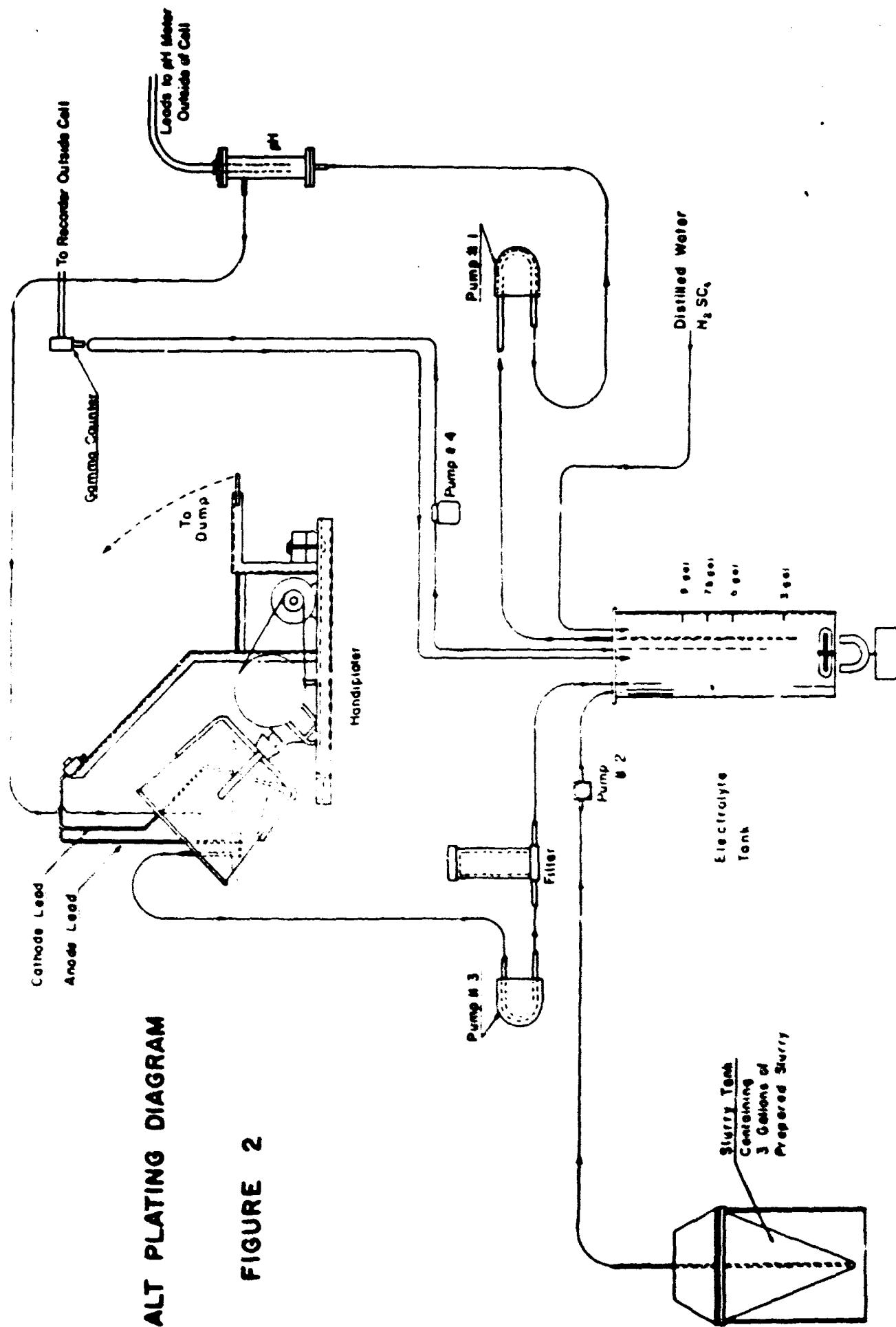
After a batch of plated pellets has been produced the remaining 10.5 gallons of electrolyte, containing 100 curies of Co-60 and 308.6 grams of total cobalt, is pumped into the cobalt slurry preparation tank and to this is added the active cobalt nitrate prepared by dissolving the Co-60 disks from two 25 curie cartridges plus ordinary cobalt sulfate sufficient to give a total of 154.3 grams of new cobalt to the solution⁹. This solution is

⁹ For our particular problem each time a new lot of slurry is made it must contain 150 curies of Co-60 and a total of 462.9 grams of cobalt. One-third of this will be new material which will be plated out in the succeeding batch, two-thirds will be in the electrolyte remaining from the electroplating of the prior batch of pellets.

heated with an immersion heater and cobalt carbonate slurry prepared as described above. A flow sheet of this operation is shown in Figure 1.

COBALT PLATING DIAGRAM

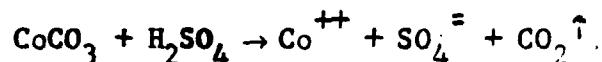
FIGURE 2



Cobalt Plating Operation

The Udylite Handiplater was chosen for its simplicity of design and because it is well suited to the plating of 1/8 inch diameter spherical steel pellets, and will hold nicely a batch of 50 pounds of these pellets. The anode was of 1/8 inch thick sheet lead which is electrolytically inert in our operation. The cathode lead was well insulated with a plastic coating except for the ball-like end which must make electrical contact with the pellet mass so that the surface of this mass becomes cathodic toward the electrolyte. If the end of the cathode lead is well buried in the mass of pellets, substantially no electrolytic deposit takes place on the cathode lead and all cobalt plated out is to be found on the pellets.

When the cobalt carbonate slurry has been divided as outlined there remains in the electrolyte tank 6 gallons of slurry with 100 curies of contained cobalt-60 and a total of 308.6 grams of total cobalt. Sufficient sulfuric acid is added to this slurry so that it dissolves according to the reaction



Distilled water is then added to bring the total volume of the electrolyte up to 7 1/2 gallons. Then sufficient sulfuric acid is added to adjust the pH of the solution to a value of 3.5. The electrolyte is now ready for the plating barrel with the barrel rotating at an appropriate speed. In going to the plating barrel the electrolyte passes a recording pH meter and controller which is interconnected to pump #2 so that when the pH is reduced below 3.5 -- because of acid formation in the electrolyte according to Equation 2 -- slurry will be pumped from the slurry tank into the electrolyte tank thus increasing the pH in the electrolyte tank to a value of 3.5 in accordance

with Equation 4. In this way the pH and the Co^{++} concentration of the electrolyte are kept constant. When all the cobalt slurry has been transferred to the electrolyte tank there will have been electrodeposited on the 50 pounds of pellets a cobalt layer 0.125 mils thick containing 50 curies of cobalt-60.

The slurry tank is constructed in the shape of a cone so that the slurry can be completely transferred to the electrolyte tank. During the plating operation there will be some settling of the slurry in the slurry tank but this is of no importance since it is pumped to the electrolyte tank only in appropriate quantities to control the pH of the electrolyte at 3.5.¹⁰ At

¹⁰ Co^{++} does not hydrolyze until the pH of the solution reaches a value of between 5 and 6. Hence the cobalt ion is completely soluble at pH = 3.5.

the end of the plating operation the volume of the electrolyte will have been increased to 10.5 gallons and thus the Co^{++} concentration at the true end of the run will be 71.4% of the concentration at the beginning of the run. This end point can be exactly effected by plating until the slurry is all run from the slurry tank into the electrolyte tank and the reading from the gamma counter at the end of the run is 71.4 percent of that at the beginning of the run. It should be noted also that if the pH alone is used to monitor the reaction that the pH of the solution increases only 0.15 pH unit in the dilution of the electrolyte from 7.5 gallons to 10.5 gallons. This variation is well within the error limit of our operation.

The inlet end of the tygon tube leading to pump #3 (which pump is set at a greater capacity than pump #1) is held at such a level in the plating barrel that it controls the level of electrolyte in the barrel. A safety device can readily be installed so that if and when the electrolyte in the

barrel exceeds the predetermined level all power is shut off and a costly and nasty clean-up job of radioactive material is avoided.

When the run is finished pump #1 is stopped and the inlet end of the hose leading to pump #3 is thrust to the lowest point of the plating barrel and all the electrolyte removed to the cobalt carbonate slurry preparation tank, Figure 1, along with 2 or 3 distilled water washings from the pellets. Thus all the active cobalt-60 is conserved; even the cobalt contained in the washings.

The anode current used in this plating operation was about 30 amperes.

The pellets can be quickly dried by washing with absolute ethyl alcohol followed by a washing with diethyl ether. After the ether wash the pellets are quickly dried with a blast of dry air.

Protective Platings

To protect the plated cobalt against abrasion and corrosion losses the cobalt plate was covered with a plated layer of nickel which in turn was covered with a plated layer of cadmium. Corrosion and abrasion tests of the finished product confirmed the chemical and physical stability of the product in the outdoors environment in which the pellets were to be used.

Briefly, the whole plating process was as follows - all processes being carried out in 50 pound lots in the Udylite Handiplater.

1. The pellets as received from the supplier were cleaned by tumbling in the plater for 15 minutes in Oakite solution, 1 pound to 2-1/2 gallons of water, then thoroughly washed.
2. The cleaned pellets in the barrel were made anodic in 0.1 molar H_2SO_4 for 1 minute; 10 amperes current; then washed and immediately copper plated.

3. The copper plating bath was Udylite BUF-R-Brite #30 electrolyte of the following detailed composition:

BUF-R-Brite Salt	13.6 oz/gallon
Sodium Cyanide	1.0 oz/gallon
Potassium Hydroxide	2.5 oz/gallon
Brightener #10	1% by volume
Addition Agent #20	5% by volume
Brightener #30	2.5% by volume

The anode was cast copper anode balls with 5 balls being used in the anode basket. Plated: 6 hours at 30 amps.

Copper layer is about 0.25 mils thick.

4. Cobalt plating is described above.

5. The nickel plating electrolyte was of the Watt's type and constituted as follows:

Nickel Sulfate	(NiSO ₄ .6H ₂ O)	32 oz/gallon
Nickel Chloride	(NiCl ₂ .6H ₂ O)	4 oz/gallon
Boric Acid	(H ₃ BO ₃)	2 oz/gallon

Anode: Cast nickel. Current: 30 amperes for 6 hours. Plate is about 0.25 mils thick. Product was washed with distilled water.

6. The cadmium plate was made from an electrolyte of a proprietary nature obtained from the Udylite Corporation.

Udylite Bry-Cad. Salt #153	1 pound/gallon
Sodium Cyanide	3 oz/gallon
Udylite Bry-Cad Brightener #22	5% by volume

The anode was cadmium balls held in an anode basket.

Current: 40 amperes for 6 hours. Deposit thickness about 0.5 mils. Complete washing and drying was accomplished by use of

for p 12
water, alcohol, ether, dry air.

In summary:

1. The product was entirely satisfactory for the intended use, and many other uses can be conceived for a product of this nature, it being possible to fabricate from such pellets radiation sources of specified intensity and shape.
2. The product is stable in most environments against removal of cobalt-60 either by abrasion or by chemical corrosion.
3. By making heavy platings and by using an active nickel anode substantially all the Co⁺⁺ can ultimately be plated out of the residual bath onto the iron pellets. This comes about because Co and Ni will plate out as an alloy with the plating being cobalt rich as compared to the electrolyte.
4. Using a suitable "cell" or "cave", now extensively used in radiation laboratories, one can carry out the operation without hazard to the operating personnel.
5. The project was not carried to completion. However, we did assemble all the equipment and made full runs with tracer amounts of cobalt-60 and demonstrated that the program was feasible from all standpoints.